



Short communication

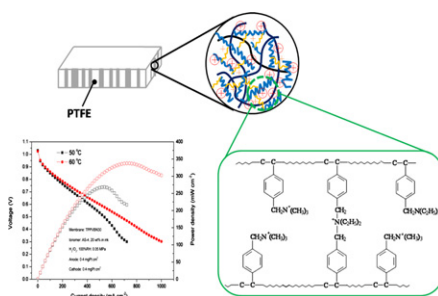
High-performance alkaline fuel cells using crosslinked composite anion exchange membrane

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HIGHLIGHTS

- ▶ A crosslinked composite membrane is successfully prepared by a feasible route.
- ▶ The composite membrane exhibits high ionic conductivity and excellent stability.
- ▶ The fuel cell with the crosslinked composite membrane shows excellent high power out.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 July 2012

Received in revised form

19 August 2012

Accepted 20 August 2012

Available online 27 August 2012

Keywords:

Fuel cells

Composite membrane

Anion exchange membrane (AEM)

Ionic conductivity

Polymer

ABSTRACT

A crosslinked composite anion exchange membrane was first prepared for anion exchange membrane fuel cell (AEMFC) application by a feasible route. The membrane exhibited high ionic conductivity, excellent dimensional and thermal stability. An AEMFC assembled with the crosslinked composite membrane showed high power output and promising cell durability. This result indicates that the crosslinked composite membrane has potential for AEMFC application.

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1. Introduction

Fuel cell technology has been recognized as a promising clean power source in future energy system which has been undergoing revolutionary developments in the last few decades [1–3]. Among the different types of fuel cell systems, proton exchange membrane fuel cell (PEMFC) is the most developed [4,5]. Despite of the great success, there are still many challenging barriers that hinder their

way of popularization and are difficult to overcome. Among the limitations, the dependence on noble metal catalyst is the critical one. As we know, Nafion is a strong acid in nature, which only allows noble metals to be used as the compatible catalyst, thus increasing the cost hinders their further application. To solve this problem, AEMFC has begun to attract a lot of attention recently, because some non-noble metals with high kinetic activity for both the fuel oxidation and oxygen reduction in alkaline environment can be applied [6,7].

As a critical component of an AEMFC, AEMs play an important role in the development of the AEMFC. The high hydroxide

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conductivity, good stability and mechanical strength of the anion exchange membranes are essential for ensuring sustainable and durable operations of the AEMFC. Many groups have developed different AEMs [8–13]. However, the resulted AEMs usually suffer from poor mechanical strength under a humidified condition after incorporating anionic sites by chloromethylation and quaternization. If the degree of quaternization is high, despite high conductivity, the obtained polymer may suffer from poor mechanical properties and be not stable in long fuel cell operation. To avoid the dilemma between ionic conductivity and mechanical stability, two methods are mainly applied including crosslinking and composite membrane reinforcement technique. Recently, crosslinking technique advances in AEMs area have been reported by many researchers. For example, Na's and Zhuang's group have reported AEMs by a simple self-crosslinking strategy, the crosslinked membranes decrease swelling ratio and enhance membrane stability [14,15]. Coates and co-workers have reported the synthesis of a series of cross-linked AEMs through the ring-opening metathesis polymerization of tetraalkylammonium-functionalized cyclic olefins [16,17]. However, these membranes have to reduce ion exchange capacity due to ensuring membrane mechanical strength and stability, so the ionic conductivity of the membrane is limited and then the AEMFC cannot achieve high power output. Another enhanced membrane method is reinforcement technique. Porous PTFE membrane has been adopted as supporting material due to its high mechanical strength, thermal and chemical stability, dimensional stability, lower cost and availability of thinner membranes. PTFE reinforcement technique is considered as one of the most effective methods to increase membrane mechanical strength, especially in fabricating reinforced proton exchange membranes [18]. For example, PTFE reinforced Nafion composite membranes have been reported for years [19,20].

There are still few reports on PTFE based AEMs [21,22]. Herein we report a high performance anion exchange membrane

fabrication which combines crosslinking with composite membrane reinforcement technique. Polyvinyl benzyl chloride, PVBC which is a linear polymer with more chloromethyl group in nature, can provide more ionic exchange group (after quaternization), so we choose PVBC as the membrane backbone. However, the quaternized polyvinyl benzyl chloride (QPVBC) become brittle after casting membrane, so the PTFE membrane is used to prepare composite membranes with improving physical and chemical properties. On the other hand, the linear polymer QPVBC is not stable and will collapse and dissolve from the PTFE membrane in hot water (found in experimental process). In order to achieve membrane chemical stability, here we also utilized a self-crosslinking reaction to prepare the AEM. Diethylamine (DEA) as a crosslinking agent has been reported in the reference [15]. This method makes the process of membrane preparation simpler and does not induct additional crosslinking agent. The prepared cross-linked composite membrane structure is illustrated in Fig. 1 (denoted as TPPVBN30), which is evaluated as the AEM in terms of its ion conductivity, mechanical property and fuel cell performance.

2. Experimental

2.1. Crosslinked composite membrane fabrication

Polyvinyl benzyl chloride, PVBC (Sigma Aldrich) was dissolved in *N,N*-dimethylformamide (DMF) to form a 5% solution, then dropped diethylamine into the solution (30 mol% of the benzyl chloride group on PVBC) at 40 °C and stirred the solution for 4 h. Cooling down the reaction system to 30 °C, then the solution was quaternized by bubbling trimethylamine (Me_3N) for 1 h at 65 °C with stirring. The solution was denoted PPVBN30.

The obtained PPVBN30 solution in DMF was mixed with a certain amount of ethanol and stirred for 24 h to form

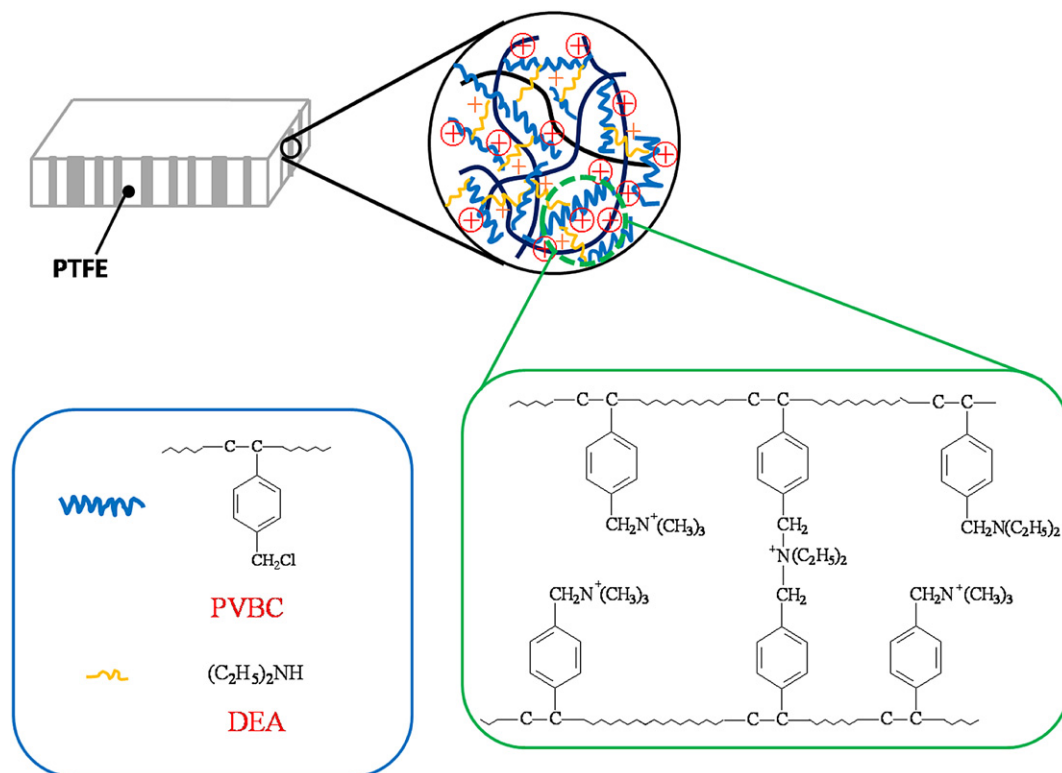


Fig. 1. Schematic structure of the prepared TPPVBN30 membrane.

a homogeneous solution. Meanwhile, to improve the wettability of the PTFE membrane in DMF, the PTFE membrane was immersed in anhydrous ethanol for 24 h. After that, the above solution was cast onto the swelled PTFE membrane to prepare the composite membrane. The membrane was heated in an oven at 60 °C for 24 h to remove the solvent, and the resulting membrane was further dried in a vacuum at 80 °C for 12 h. Then, the membrane was detached from the glass and immersed into 33 wt% TMA water solution for 24 h at room temperature to react with residual benzyl chloride group absolutely. The conversion from Cl^- form to OH^- form was achieved by leaving the resulted membranes in 1 M KOH for 24 h at room temperature. The OH^- exchanged membrane was washed with DI water until pH of 7 was reached.

2.2. Characterizations

ATR-FTIR of the prepared membranes was obtained on a JASCO FT-IR 4100 spectrometer with an ATR accessory containing a Ge crystal with a wavenumber resolution of 4 cm^{-1} and the range of $600\text{--}4000\text{ cm}^{-1}$.

2.3. Ion exchange capacity, swelling behavior and mechanical strength

The ion exchange capacity (IEC) of the membranes was determined by the titration method. The membranes in OH^- forms were soaked in 0.01 M HCl solution for 48 h at 30 °C. Subsequently, HCl was titrated against a 0.01 M aqueous solution of NaOH with phenolphthalein as the indicator. The IEC was calculated as follows

$$\text{IEC} = \frac{M_{\text{o,HCl}} - M_{\text{e,HCl}}}{m} \quad (1)$$

where $M_{\text{o,HCl}}$ and $M_{\text{e,HCl}}$ are moles of HCl before and after titration with NaOH, respectively, and m is the weight of the membrane.

The swelling ratio could be calculated as follows

$$\text{Swelling ratio}(\%) = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (2)$$

The length of sample was taken in the OH^- form when they were fully hydrated and dried, respectively. The drying of samples was carried out at 60 °C for 24 h.

The mechanical property of the membranes was measured with a WDW Electromechanical Universal Testing Machine at room temperature. The membrane specimens were of 10 mm width and tested using a programmed elongation rate of 50 mm min^{-1} . Before the measurements, the membrane samples were kept in DI water at room temperature overnight and water on the surface was absorbed with filter paper.

2.4. Ionic conductivity measurement

The ionic conductivity was determined by using a cell with a pair of pressure-attached copper electrodes coated with gold. The resistance of the membrane was measured by using electrochemical impedance spectroscopy (EIS), with a Solartron 1260 frequency response analyzer coupled to a Solartron 1287 potentiostat. Signal amplitude of 10 mV in the frequency range of 1 MHz–0.1 Hz was applied. Before the measurements, the membranes were kept in DI water to minimize its exposure to ambient CO_2 . The membrane sample was taken out quickly, and then sealed between two plates with electrodes of testing fixture, which was placed in DI water to keep a relative humidity of 100%. Moreover, DI water was refreshed before each measurement. The

membrane conductivity (σ , S cm^{-1}) could be calculated by the following equation:

$$\sigma = \frac{L}{RS} \quad (3)$$

where L (cm) is the distance between the working electrode and the reference electrode, S (cm^2) is the membrane cross sectional area, and R (Ω) is the membrane resistance, which is obtained by simulating from the AC impedance data (Ω).

2.5. Preparation of MEA and fuel cell tests

MEA was prepared as follows, a commercial catalyst Pt/C (70%, JM Co.) was mixed with a certain amount of water, isopropyl alcohol and AS-4 ionomer solution (Tokuyama Co.), and then sonicated to obtain a homogeneous ink. The above mentioned catalyst ink was sprayed onto the composite membrane to obtain a catalyst coated membrane (CCM). The Pt loading of the anode and cathode were both 0.4 mg cm^{-2} and the weight ratio of catalyst to ionomer was 80:20. The above-obtained CCM was hot-pressed between two gas diffusion layers (Toray-060) to obtain the membrane electrode assembly (MEA) at 60 °C, 1 MPa for 2 min. Fuel cells with 5 cm^2 active area were assembled using stainless steel end-plates. When testing the fuel cell performance, the cell temperature was set at certain temperature with H_2 and O_2 at 100% relative humidity (RH). The flow rate of H_2/O_2 was $100/200\text{ ml min}^{-1}$ at 0.05 MPa, respectively.

3. Results and discussion

The structure of TPPVBN30 was confirmed by ATR-FTIR (Fig. 2). The spectra showed the peaks between 2918 and 2850 cm^{-1} , peaks was the characteristics of $-\text{CH}_3$, $-\text{CH}_2$ groups and a peak at 1386 cm^{-1} was identified to C–N stretching vibration, the peak around 3300 cm^{-1} by characteristic of the O–H and N–H bond, the peaks at 1207 and 1150 cm^{-1} originated from C–F bond of PTFE. It is also noted that peak at 1207 cm^{-1} originating from the TPPVBN30 membrane shifted due to the interaction with the incorporated species, maybe because of shielding by the neighboring strong absorptions.

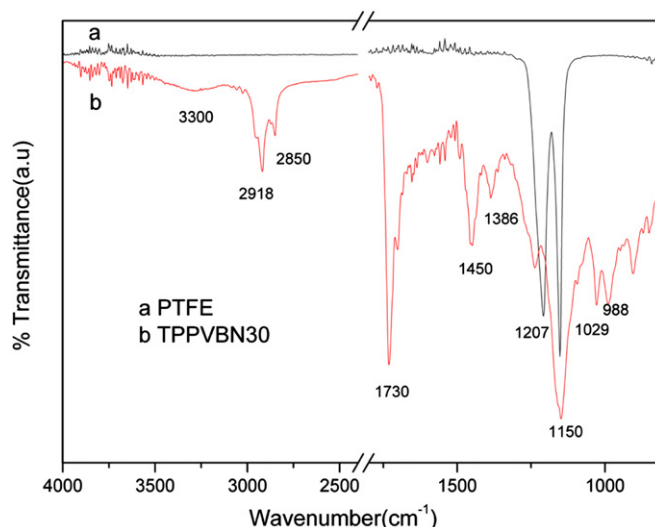


Fig. 2. FT-IR spectra of PTFE and TPPVBN30 composite membrane.

Table 1
Membrane properties of TPPVBN30 composite membrane.

Sample	DEA%	IEC (meq g ⁻¹)	Swelling ratio ^a (%)	Mechanical strength ^b (MPa)	Elongation at break ^b (%)	Thickness (μm) ^b
TPPVBN30	30	2.29	13.3	18.5	19.2	26

^a The swelling ratio was measured at 25 °C.

^b The sample was measured at room temperature and in dry state condition.

The ionic conductivity is a critical parameter for the ion exchange membranes in fuel cells. To achieve high ionic conductivity of the TPPVBN30 membrane, two strategies were designed in our experiments. First, the PVBC polymer with high chloromethyl group (leading to high $-NR_3^+$ degree) was chosen, so we obtained the TPPVBN30 membrane with high ion exchange capacity (IEC, 2.29 mmol g⁻¹) (Table 1). In addition, the PTFE membrane as the substrate not only insured good membrane stability and strength but mimicked the microphase separated morphology of some proton exchange membranes, facilitating ion transport across the membrane. Fig. 3 showed the ionic conductivities of the TPPVBN30 membrane along with the ionic conductivities of Nafion 211 membrane (measured under identical conditions). The ionic conductivity was substantially higher for the TPPVBN30 membrane (0.032 S cm⁻¹ at 25 °C) than for other quaternary ammonium types of AEMs such as QAPS (0.02 S cm⁻¹ at 30 °C) [8], QPPESK (0.005 S cm⁻¹ at 30 °C) [9], QPEK-C (0.0016 S cm⁻¹ at 20 °C) [10], crosslinked SPES-OH (around 0.019 S cm⁻¹ at 20 °C) [14], crosslinked xTQAPS (around 0.018 S cm⁻¹ at 20 °C) [15], radiation-grafted ETFE (0.034 S cm⁻¹ at 50 °C) [23], QPMBV-APE (0.043 S cm⁻¹ at 80 °C) [24], and qPVB/OH⁻ (0.021 S cm⁻¹ at 25 °C) [25]. Unlike other homogeneous AEMs, high dimensional stability (mechanical strength) and high ionic conductivity (usually high IEC) were very difficult to be achieved simultaneously. Though the TPPVBN30 membrane exhibited high IEC, it also had excellent dimensional stability due to PTFE membrane limitation and crosslinked effect. As is shown from Table 1, the swelling ratio of the prepared composite membrane is 13.3% at 25 °C.

Furthermore, the conductance stability of the TPPVBN30 membrane was also investigated in hot water. As demonstrated in Fig. 4, the ionic conductivity of the TPPVBN30 membrane at 80 °C water showed no ionic conductivity decrease over a test period of

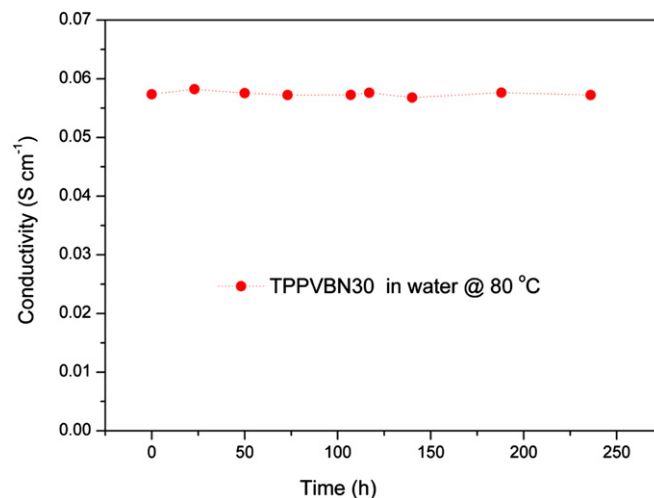


Fig. 4. Stability test of ionic conductivity in 80 °C water.

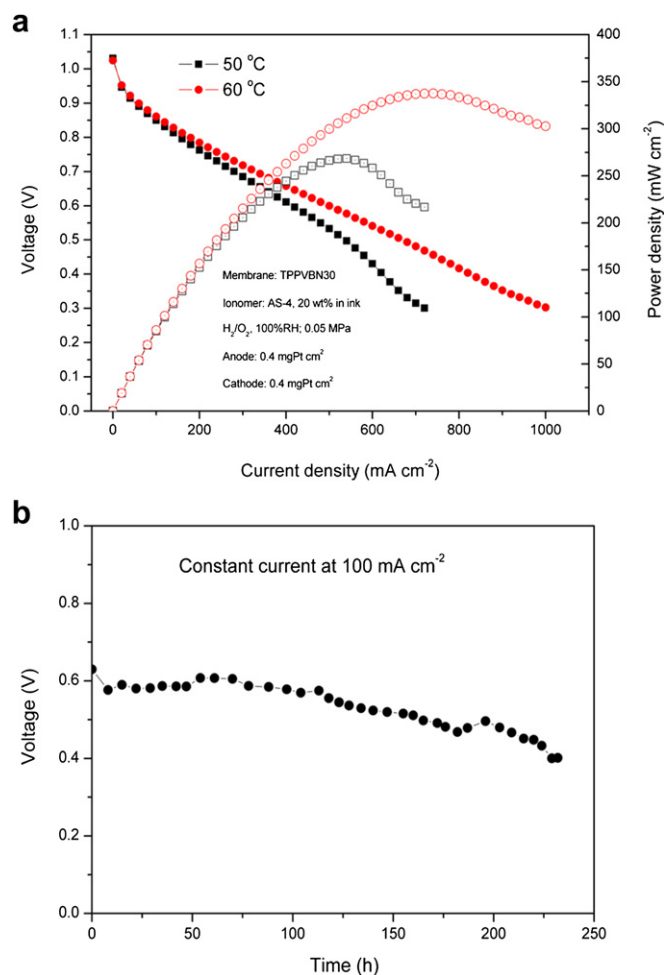


Fig. 5. *I*–*V* polarization curves and stability test of the fuel cell with TPPVBN30 membrane: (a) Test conditions: catalyst loading 0.4 mg cm⁻² (based on Pt) for the anode and the cathode, flow rate 0.1 L min⁻¹ and 0.2 L min⁻¹ for H₂ and O₂, respectively, back pressure 0.05 MPa and humidity 100% RH, (b) Test conditions: cell temperature 50 °C, catalyst loading 0.4 mg cm⁻² (based on Pt) for the anode and the cathode, flow rate 0.1 L min⁻¹ and 0.2 L min⁻¹ for H₂ and O₂, respectively, no back pressure and humidity 100% RH.

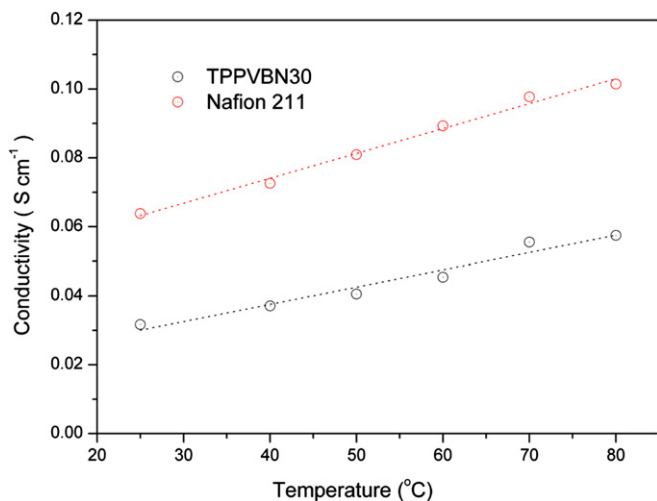


Fig. 3. Temperature dependence of ionic conductivities of TPPVBN30 and Nafion 211 membranes.

Table 2The peak power density of H₂–O₂ AEMFC reported.

AEMs	Thickness [μm]	P_{max} [mW cm^{-2}]	Cell temperature [$^{\circ}\text{C}$] (back pressure, [kPa])	Pt loading [mg Pt cm^{-2}]	Ionomer
TPPVB30 (this work)	26	338	60 (0.05)	0.4	AS-4
TPQPOH152 [26]	50	258	70 (0.25)	0.2	TPQPOH124
Radiation-grafted AEM [27]	80 (wet)	210	50 (0)	0.5	t-PVBTMACI
FAA [28]	70	200	80 (0.25)	0.5	TPQAOH
QPMBV-APE [24]	50	180	70 (0.1)	0.4	QPMBV
qPVB/OH [−] [25]	50	156	15 (0)	0.8	qPVB/OH [−]
PTFE-QDPSU [22]	30 (wet)	146	50 (0)	0.5	QDPSU
QAPS [8]	40	100	60 (0)	4	QAPS

234 h. Such excellent thermal stability should be attributed to the PTFE membrane reinforcement and a strong self-crosslinked network.

Although the TPPVB30 membrane had been shown with high ionic conductivity, excellent dimensional and thermal stability, the most practical evaluation was the performance of the AEMFC. Prior to the fuel cell performance test, MEA was fabricated following the standard procedure as it was described in the Experimental section by using the TPPVB30 membrane (26 μm in dry state, OH[−] form) as the electrolyte and AS-4 (Tokuyama Co.) in an isopropyl alcohol solution as the anion conductive ionomer. Pt was used as a catalyst with a loading of 0.4 mg cm^{-2} . The performance of fuel cell with the TPPVB30 membrane was tested at 100% relative humidity (RH) at various temperatures and pressure of 0.05 MPa. Fig. 5 (a) showed the polarization curves of H₂/O₂ AEMFC with the TPPVB30 membrane at 50 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$, respectively. The open circuit voltages (OCVs) were 1.03 V, indicating that the TPPVB30 membrane could well separate the reactant gases. The initial voltage drop was mainly attributable to an activation loss of the interfacial electrochemical charge-transfer reaction in the catalyst layer. After the initial activation loss, the fuel cell voltage decreased gradually with an increase in current density. At 50 $^{\circ}\text{C}$, the current density reached 800 mA cm^{-2} , and fuel cell delivered a peak power density of 268 mW cm^{-2} at 0.5 V. When temperature raised to 60 $^{\circ}\text{C}$, the maximum power density of 348 mW cm^{-2} could be obtained at 0.5 V, the current density reached 1000 mA cm^{-2} . This is almost the best performance reported for AEMs (Table 2).

To date, little investigation on membrane durability has been conducted on the AEMFCs. However, this test is of great importance for the long term prospect of the AEMFCs. In this work, AEMFC durability with the TPPVB30 membrane was also tested. Fig. 5 (b) showed the cell performance at a continuous operating period of 232 h. We are aware that the above durability is still incomparable with that of PEMFCs and still far from meeting the requirements of real applications, but it is respectable and encouraging for AEMFCs whose durability is very challenging.

4. Conclusions

A crosslinked composite anion exchange membrane was designed and fabricated for AEMFC application. Membrane not only had high IEC and ionic conductivity, but also showed excellent dimensional and thermal stability. The AEMFC with the crosslinked composite membrane showed a high performance and this is nearly the best performance reported for AEMs. The exceptional

performance and fuel cell durability reveal the great potential of the crosslinked composite anion exchange membrane.

Acknowledgments

This work was financially supported by the National High Technology Research and Development Program of China (863 Program, No. 2011AA050705), National Basic Research Program of China (973 Program, No.2012CB215500) and the National Natural Science Foundations of China (No. 21176234, No. 20876154).

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